WO0156128

Publication Title:

ENCAPSULATION OF SUPERCONDUCTING COMPOSITES

Abstract:

Methods of preparing superconducting composites for hermetic sealing. It has been found that superconducting composites may not be fully wetted by solder as made, and that the wettability of the composites can be enhanced by chemically etching the surface of the composite. In addition, it has been found that vacuum baking composites prior to soldering may improve coverage.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
2 August 2001 (02.08.2001)

PCT

(10) International Publication Number
WO 01/56128 A2

(51) International Patent Classification[7]: H02H

(21) International Application Number: PCT/US01/01762

(22) International Filing Date: 18 January 2001 (18.01.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/488,740 20 January 2000 (20.01.2000) US
09/548,215 12 April 2000 (12.04.2000) US

(71) Applicant: AMERICAN SUPERCONDUCTOR CORPORATION [US/US]; Two Technology Drive, Westborough, MA 01581 (US).

(72) Inventors: CHRISTOPHERSON, Craig, J.; 26 Anthony Drive, Holden, MA 01520 (US). OUELLETTE, Deborah, L.; 230 Keys Road, West Brookfield, MA 01585 (US). OLEN, David, M.; 389 Reservoir Street, Holden, MA 01520 (US). DE SANTOS, Thomas; 320 Morton Street, Stoughton, MA 02072 (US). LOONG, Sy-Jeng; 15 Butterfield Drive, Westborough, MA 01581 (US). PODTBURG, Eric, R.; 28 Sherwood Road, Natick, MA 01760 (US). BUCZEK, David, M.; 81 Tisdale Road, Dover, MA 02030 (US). TANNER, Michael, A.; 8 Brickyard Lane, Westborough, MA 01581 (US). PEREIRA, John, B.; 377 Bryant Street, Cumberland, RI 02864 (US). PARKER, Donald, R.; 4 Saratoga Street, Randolph, MA 02368 (US). CHRYSSANTHACOPOULOUS, Peter; 71 Blanchette Drive, Marlboro, MA 01752 (US). WALSH, Christine; 9 Thoreau Court, Unit #17, Natick, MA 01760 (US).

(74) Agent: NUGENT, Elizabeth, E.; Choate, Hall & Stewart, Exchange Place, 53 State Street, Boston, MA 02109 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/56128 A2

(54) Title: ENCAPSULATION OF SUPERCONDUCTING COMPOSITES

(57) Abstract: Methods of preparing superconducting composites for hermetic sealing. It has been found that superconducting composites may not be fully wetted by solder as made, and that the wettability of the composites can be enhanced by chemically etching the surface of the composite. In addition, it has been found that vacuum baking composites prior to soldering may improve coverage.

Encapsulation of Superconducting Composites

The present application is a continuation-in-part of copending and commonly assigned U.S. Application No. 09/488,740, filed January 20, 2000, which is incorporated herein by reference.

Field of the Invention

The present invention is related to methods of preparing composites for encapsulation in a sealing material.

Background of the Invention

High temperature superconductors (HTS materials) have increasing utility as power conductors, fault current limiters, and other applications. Since HTS materials are generally brittle oxides, it is common to produce them in composite form, wherein superconducting filaments are supported by a noble metal matrix. The matrix is most commonly silver-based, but any metal or alloy which will withstand superconductor processing conditions and which does not act to poison the superconductor may be used.

It has been observed that in use, superconducting composites often exhibit "ballooning." When the composite is immersed in liquid nitrogen or another cryogen suitable for achieving superconducting properties, a certain amount of cryogen collects in interstices between the matrix and the superconducting filaments. When the composite is allowed to return to room temperature, the cryogen expands and causes portions of the composite to deform to form balloons. This deformation subjects the delicate superconducting filaments to fatigue and possibly fracture, degrading or destroying superconductor filaments. A strong need thus exists for a method of preventing ballooning from occurring. Thus, methods of sealing a superconducting composite to prevent cryogen infiltration are needed.

While noble metal matrices provide some mechanical support to superconducting filaments in a composite, it is often desirable to laminate further material to the composite. For example, a stronger metal may be used to

mechanically reinforce a composite wire while maintaining a low cross-sectional area, or a thermally conductive material may provide improved heat transfer out of the composite.

Summary of the Invention

The present invention provides improved methods of preparing composites for encapsulation and/or lamination. When a superconducting composite is to be laminated by soldering it to another material (*e.g.*, a metal tape which can provide mechanical and/or thermal stabilization), it is important that the laminate be sealed against any infiltration by liquid cryogen to prevent ballooning, and further that it be in good thermal and mechanical contact with the solder in order to avoid the creation of hot spots or stress concentrations. Similarly, when a composite is protectively encapsulated (*e.g.*, with solder or with a polymer), the encapsulating material should be free of defects that might compromise the integrity of the seal. Also, when forming multistrand cables, solder or another material may be used to hold the strands together, and again, a good contact and wettability between the solder and the strands should be achieved.

In one aspect, the invention comprises methods of preparing superconducting composites for lamination, encapsulation, or any other process that requires wetting of the composite by a liquid (*e.g.*, a liquid metal). The methods comprise removing a thin layer of matrix material to expose a surface having a low concentration of oxide particles. The layer may be removed, for example, by chemical etching or by electrolytic cleaning. If it is removed by etching, the etchant may be, for example, nitric acid, hydrochloric acid, hydrofluoric acid, sulfuric acid, ferric chloride, ammonia, a caustic solution, a mixture of these, or any other chlorinated or fluorinated solvent, and may contain other salts such as ammonium bifluoride. The thin layer may be on the order of 0.013 mm thick, or as thick as can be achieved without excessively degrading the properties of the superconductor (*e.g.*, degrading the critical current by more than about 10%). The exposed surface may have a wettability in solder of at least 250 μN/mm, 300 μN/mm, or 350 μN/mm. When the thin layer is removed electrolytically, an electrolyte such as nitric acid, hydrochloric acid, hydrofluoric acid, sulfuric acid, sodium hydroxide, ferric chloride, ferrous

chloride, ferric fluoride, or ferrous fluoride may be used. The removal process may leave the exposed surface at least 97% free of foreign particles, at least 99% free, at least 99.5% free, or at least 99.8% free.

In another aspect, the invention comprises methods of preparing superconducting composites for lamination, encapsulation, or any other process that requires wetting of the composite by a liquid (*e.g.*, a liquid metal). The methods comprise exposing the superconducting composite to an environment adapted to remove liquids from the exposed surface, such as a vacuum (*e.g.*, a vacuum of about 10 millitorr) or an inert environment. The environment may include an elevated temperature (*e.g.*, a temperature between about 100°C and about 200°C).

In yet another aspect, the invention comprises methods of preparing superconducting composites for lamination, encapsulation, or any other process that requires wetting of the composite by a liquid (*e.g.*, a liquid metal). The methods comprise both removing a thin layer as described above, and removing liquids by exposure to a dessicating environment as described above.

By "noble metal" as it is used herein, it is meant any metal whose reaction products are thermodynamically unstable under the reaction conditions employed relative to the desired superconducting ceramic, or which does not react with the superconducting ceramic or its precursors under the conditions of manufacture of the composite. A noble metal matrix may be a metal different from the metallic elements of the superconducting ceramic, such as silver, gold, or their alloys, or it may be a stoichiometric excess of one of the metallic elements of the superconducting ceramic, such as copper.

By "superconducting ceramic" as it is used herein, it is meant the oxide superconductor intended for eventual use in the finished article, or any precursor thereof. Typically, the desired final oxide superconductor is selected for its superior electrical properties, such as high critical temperature or critical current density. The desired oxide superconductor is typically a member of a superconducting oxide family which has demonstrated superior electrical properties, for example, BSCCO 2223 (including $(Pb,Bi)_{2.1}Sr_2Ca_2Cu_3O_{10+x}$ and $Pb_{0.2}Bi_{1.9}Sr_2Ca_2Cu_3O_{10+x}$) or BSCCO 2212 in the BSCCO family, or YBCO 123 in the YBCO family. By "precursor" is meant any material that can be converted to an oxide superconductor upon application

of a suitable heat treatment. Precursors may include any combination of elements, metal salts, oxides, suboxides, oxide superconductors which are intermediate to the desired oxide superconductor, or other compounds which, when reacted in the stability field of a desired oxide superconductor, produces that superconductor. For example, there may be included elements, salts, or oxides of copper, yttrium, and barium for the YBCO family of oxide superconductors; elements or oxides of copper, bismuth, strontium, and calcium, and optionally lead, for the BSCCO family of oxide superconductors; elements, salts, or oxides of copper, thallium, calcium and barium or strontium, and optionally, bismuth and lead, for the thallium (TBSCCO) family of oxide superconductors; elements, salts, or oxides of copper, mercury, calcium, barium or strontium, and optionally, bismuth and lead, for the mercury (HBSCCO) family of oxide superconductors. The YBCO family of oxide superconductors is considered to include all oxide superconductors of the type comprising barium, copper, and a rare earth, such as yttrium, lanthanum, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, or lutetium. By "oxide superconductor intermediate to the desired oxide superconductor" is meant any oxide superconductor which is capable of being converted to the desired oxide superconductor. The formation of an intermediate may be desired in order to take advantage of desirable processing properties, for example, a micaceous structure amenable to texturing, which may not be equally possessed by the desired superconducting oxide. Precursors are included in amounts sufficient to form an oxide superconductor. In some embodiments, the precursor powders may be provided in substantially stoichiometric proportion. In others, there may be a stoichiometric excess or deficiency of any precursor to accommodate the processing conditions used to form the desired superconducting composite. For this purpose, excess or deficiency of a particular precursor is defined by comparison to the ideal cation stoichiometry of the desired oxide superconductor. Thalliation, the addition of doping materials, including but not limited to the optional materials identified above, variations in proportions and such other variations in the precursors of the desired superconducting oxides as are well known in the art, are also within the scope and spirit of the invention.

Brief Description of the Drawing

The invention is described with reference to the several figures of the drawing, in which,

Figures 1a and **1b** show defects which may be observed in laminated superconducting composites;

Figures 2a and **2b** are photomicrographs of a superconducting composite before and after chemical etching treatments according to the invention;

Figure 3 plots wetting balance of superconducting composites before and after chemical etching treatments according to the invention; and

Figure 4 plots wetting balance of pure silver and pure copper.

Detailed Description

The present invention provides improved methods of laminating a material to a superconducting composite. These methods allow solder to wet the surface of a metal matrix much more effectively, and also reduce or eliminate outgassing during soldering, thereby reducing pinholes in the solder that can allow liquid cryogen to penetrate the composite and cause ballooning.

It has been found that very small tunnels (**Figure 1**) and similar defects can form in solder fillets during a lamination process, which can provide pathways for cryogen to infiltrate the superconducting composite to cause ballooning. These tunnels can also lead to nonuniform heat transfer when the superconducting composite carries a sufficiently high current that resistive heating can occur (as when superconducting composites are used as fault current limiters). In addition, defects can cause stress concentrations that may adversely affect the properties of the composite. The inventors have discovered that these tunnels and other defects may be attributed to oxide particles and/or other defects on the surface of the composite before the solder is applied, and have developed novel techniques for removing these deposits.

Superconducting composites are often formed by first forming a precursor composite, which is then subjected to heat treatment (usually under an oxidizing atmosphere) to produce the desired superconductor composite. The oxide-powder-in-tube (OPIT), metal precursor (MP), and coated conductor (CC) routes of superconductor formation are examples of such processes. The precursor composite

is generally converted into the final desired superconducting composite before lamination, to avoid damaging the solder layer or allowing it to poison the oxide superconductor.

It is desirable to wind precursor composite tapes on a mandrel or cassette before heat treating, so that a large quantity of material can be heat treated in a batch process. One problem with this technique is self-sticking, wherein adjacent surfaces of the metal matrix bond to one another during the heat treatment. It can be very difficult to separate the tapes after heat treatment without causing mechanical damage to the composite.

Commonly assigned U.S. Patent No. 5,952,270 to Hughson, *et al.*, and copending and commonly assigned U.S. Patent Application No. 09/309,220, filed May 10, 1999 (both of which are incorporated herein by reference) describe a system for preventing mechanical damage in heat treating precursor composites, by applying a separating agent to the tape surface before heat treating. This separating agent may be, for example, a porous coating or a powder (*e.g.*, Zr_2O_3, MgO, or CuO powder) which separates the adjacent metal layers to prevent sticking. While the separating agent is preferably a material which is relatively easy to remove from the composite surface after heat treating, small quantities of the agent often remain even after determined efforts to remove them. For example, even after cleaning with a regimen of air jets, vacuum treatments, mechanical abrasion, and ultrasonic cleaning, some particles of MgO powder have been observed to remain on the surface of the material. Partially embedded particles have also been observed after these treatments.

In addition, oxide and other particles may form on the surface of the composite during heat treatment. A very common matrix material is silver (or silver alloys). Even high-purity silver usually contains some amount of "tramp" copper as an impurity. It has been observed that in the high temperatures and oxidating conditions used to convert precursor composites into superconducting composites, this copper may segregate to the surface to form copper oxide. In addition, silver is vulnerable to trace amounts of sulfur in the air, forming a silver sulfide skin (tarnish) on its surface.

Copending and commonly assigned U.S. Patent Application No. 09/240,998, filed Feburary 1, 1999 and PCT publication WO99/40633 (both of which are

incorporated herein by reference) disclose methods of alloying a noble metal matrix such as silver with other elements such as gallium, tin, antimony, or other suitable materials by a diffusion process. This diffusion process may also leave behind some amount of an oxide of the alloying element on the surface of the composite.

Any of these foreign particles or oxide/sulfide layers may be further embedded into the surface by subsequent rolling operations, rendering them even more difficult to remove without damaging the superconductor. Further, it has not previously been recognized that any need existed to remove more of the particles than can be removed by conventional methods such as water or air knives, ultrasonic cleaning, mechanical scrubbing, and the like. The present invention comprehends the discovery that even a small concentration of these particles may serve as a source of "tunnel" defects in a solder layer when such a composite is laminated.

In addition, the inventors have found that tunnel defects may also be associated with composite defects in which the matrix does not completely cover the superconducting filaments ("perforations"). Tunnels associated with perforations may be those most vulnerable to ballooning, since they provide a pathway for the cryogen to reach the superconducting composite at a point where the superconducting filaments are not fully protected by the metal matrix from cryogen infiltration. We have found that this type of defect can be markedly reduced by vacuum baking the composite before lamination, as described below.

In a typical desired configuration for a laminated composite, the superconducting composite is surrounded by solder (or other encapsulating material), which in turn bonds it to stabilizing elements. The stabilizing elements may be designed to provide mechanical support and/or extra thermal mass to the composite, and may comprise materials such as stainless steel, copper, nickel, or various other metals and alloys. Other configurations may be preferred in certain applications; for example, the invention may be practiced in connection with the "face-to-face" arrangement of coated conductors described in U.S. Provisional Patent Application No. 60/145,468, filed July 23, 1999, which is incorporated by reference herein.

When a composite is laminated without the special treatments of the invention, the solder coating often contains defects such as those shown in **Figures 1a** and **1b**. As shown in **Figure 1a**, narrow tunnels **18** provide a pathway for cryogen to infiltrate

the superconducting composite **10** through solder fillets **16**, thereby causing the laminated composite to exhibit ballooning in use. **Figure 1b** shows a "face-to-face" coated conductor configuration, comprising two coated conductors, each comprising a substrate **20**, a buffer layer **22**, a superconductor layer **24**, and a cap layer **26**. As shown, these conductors are joined by a solder layer **28** which comprises two fillets **29**. The fillets **29** may comprise tunnels **30, 32**. These may either provide a direct pathway from the exterior to the superconducting layer **24** as seen at **30**, or may reach to the (usually silver) cap layer **26** as shown at **32**. If a perforation exists at **34**, the cryogen may reach the superconducting layer **24**. Without wishing to be bound by any particular explanation, it is believed that the tunnels **18, 30, 32** of **Figures 1a** and **1b** can be formed both by the presence of foreign particles on the composite surface, and by small amounts of liquid which may be trapped at perforations and/or on foreign particles as the composite enters the solder bath.

Figure 2a is a photomicrograph of the surface of a composite of BSCCO filaments in a silver matrix, which has been heat treated and cleaned by conventional methods. Despite cleaning procedures significantly more stringent than those normally suggested to prepare a surface for soldering, a number of foreign particles remain. The large dark particles in the figure have been found to comprise primarily copper oxide, while the uneven "haze" of lighter gray material is mostly fine MgO particles. It is estimated that the total coverage of the surface by particles is on the order of 3-5%. According to the invention, a substantial portion of these particles are removed by removing a thin surface layer from the matrix.

In one preferred embodiment, the oxide particles are stripped from the surface by etching away a thin layer of the surface. An example of the results of this process can be seen in **Figure 2b**. This photomicrograph shows the composite of **Figure 2a** after a chemical treatment according to the invention. In this case, the composite was held in a 50/50 mixture of nitric acid and water containing 90 g/l of ammonium bifluoride. The etching solution was heated to 48°C and the matrix was held in the solution for a period of 5 sec, etching the silver matrix to a depth of about 0.013 mm (0.0005"). A comparison of **Figure 2a** and **Figure 2b** will show that a very large proportion of the foreign particles have been removed by this chemical treatment.

The particular matrix material and etching parameters used in the sample of **Figures 2a** and **2b** are exemplary only; other chemical treatments which provide similar etching of the metal matrix may also be used. It is expected that solutions comprising chloride and/or fluoride ions will be effective for etching many common matrix materials; known etchants for specific materials may be found in metallurgy reference books such as the Metals Handbook (ASM International, 1998). Alternatively, other methods of removing a thin layer of matrix material, such as electrolytic cleaning or plasma etching, may also be used. It is recommended that etching be to a depth of at least half of the typical particle diameter of the surface particles, and etching may be as deep as desired without damaging a large fraction of the superconducting filaments. Some damage to surface filaments is acceptable, as long as it does not cause an unacceptable degradation in the desired properties of the superconducting composites (*e.g.*, a degradation of more than 10% in the total critical current).

Once the matrix has been etched to remove these particles, the inventors have discovered the surprising result that the wettability of the matrix (*e.g.*, by solder) is remarkably enhanced. In addition, the matrix is generally thinner and more uniform after etching. Without wishing to be bound by any particular explanation, it is believed that the enhanced wettability of the etched matrix is due to removal of the foreign particles. Despite the fact that the concentration of particles on the surface before treatment is relatively small (well within normal guidelines for a surface "clean" enough to solder), they appear to have a significant effect upon wettability of the matrix. This conclusion is supported by the determination that pure silver has a wettability similar to that of the treated samples (see **Figures 3** and **4**).

Figure 3 plots measurements of the wetting of matrix material which has been treated according to the invention. These plots were generated by measuring the force on a strip of composite material as it was dipped into a pot of molten solder, according to MIL-STD-883/TM2022 (incorporated herein by reference). Lines **110** show force (in μN/mm) vs. time (in seconds) for untreated specimens, while lines **112** show similar measurements for specimens treated according to the invention.

For the untreated specimens, it can be seen that there was a small force resisting insertion of the specimen into the solder, until the surface tension of the

molten solder was broken. A capillary action acting to pull the specimen further into the pot then built up as the specimen was inserted farther into the solder. At point **114**, the specimen was held stationary in the solder. During the time that the specimen was held in the solder (between points **114** and **116**), the force wavered considerably, indicating some instability in the wetting behavior, but eventually, at point **116**, stabilized at an equlibrium value. (Without wishing to be bound to this explanation, it is believed that this wavering is due to dewetting of the oxide particles on the surface of the material).

The untreated specimens have been found to exhibit small solder tunnels and consequent ballooning, despite the fact that they pass many conventional solderability tests, including the MIL-STD-883/TM2022 and DeVore's Solderability Index (both of which are discussed in Russell, *et al.*, "Component Solderability Guide," Electronic Industries Association, incorporated herein by reference).

In contrast, the specimens treated according to the invention exhibited significantly different behavior. There was essentially no initial resistance to insertion of the specimens into the solder at the start of the test, and the capillary force built up to a much higher level, indicating that the surface of the specimens was much more readily wetted by the solder. In addition, the instability was much reduced for two of the three treated specimens.

The wettability data for the treated and untreated composites were compared with wettability data for pure silver **118** and for pure copper **120**, as shown in **Figure 4**. While the copper and silver specimens required a greater force to break the initial surface tension of the liquid solder, because of their larger cross-sectional area, the wetting curve for pure silver is very similar to that of the treated specimens, lending support to the idea that the treatment works by exposing an uncontaminated silver (or alloy) surface.

In another example of the techniques of the invention, about 10-13 weight % Ga (with respect to Ag content) was deposited on the surface of a superconducting tape comprising BSCCO filaments in a silver sheath, using electroplating techniques and a reel to reel electroplating line. After plating, the Ga was diffused into the sheath, making a high resistance Ag-Ga solid solution alloy. After the diffusion process, a gallium oxide skin was present on the surface of the tape. This oxide layer

was chemically removed prior to subsequent lamination processing, using a 50% nitric acid / 50% deionized water solution containing 90 g/l of ammonium bifluoride. The etching solution was heated to 48°C and the diffused tape was run through the solution (maintaining a 5 sec residence time) using a reel to reel etching line. Once the tape was chemically stripped of its gallium oxide layer, it was readily soldered during the lamination process.

The lamination process was used to provide both mechanical and thermal stabilization for the strand. Using reel to reel processing machinery and a wave solder pot, the gallium post processed wire was bonded to a stainless steel stabilizer using a 50/50 lead-indium solder.

The chemical etching treatments described above provided substantial improvements to the wettability of the superconducting composite during subsequent lamination steps. In addition to or instead of this treatment, the formation of tunnel defects can also be reduced by vacuum baking the composite prior to coating it with solder. For example, exposure of a composite comprising BSCCO fibers embedded in a silver matrix to a temperature of about 100-200°C and a pressure of about 10 millitorr for about three to twelve hours has been found to significantly reduce the frequency of tunnels through solder fillets associated with perforations. After vacuum baking, the pressure chamber may be backfilled with an inert gas such as argon or nitrogen while the composite cools.

Without wishing to be bound by any particular explanation, it is believed that the exposed ceramic material at perforations, and/or any remaining foreign particles, "getter" or absorb liquid, either during solution treatment steps (*e.g.*, ultrasonic cleaning to remove surface particles, or the chemical etching steps described above), from exposure to a humid environment, or from a combination of these factors. If this liquid is not removed, it vaporizes or outgasses when the superconducting composite is immersed in liquid solder, leaving a tunnel defect in the fillet. Vacuum baking prior to lamination evaporates the liquid so that fillets form without tunnels. It will be apparent to those skilled in the art that vacuum baking is not the only treatment step appropriate for removing residual liquid; for example, a bake in an inert atmosphere such as nitrogen or argon gas could also be used, as could a room-temperature dessicating environment.

This vacuum bake step is preferably the last step before soldering, or at least is subsequent to all solution processing steps, so that all water or other liquid is removed before soldering. It is preferred that the vacuum bake conditions not be conducive to the formation of foreign particles on the surface that might interfere with wettability of the composite with the solder. For example, oxygen activity should be kept low, especially if metallic copper, gallium, or other oxidizable metals are present at the surface of the composite, to avoid forming new oxide particles after the chemical cleaning step of the invention has been completed. Similarly, care should be taken that silver sulfide does not form on the surface of the superconducting composite, for example by bagging the wires in an inert atmosphere.

While chemical cleaning and vacuum baking combine to produce a particularly high-quality composite, each may beneficially be used alone in treatment of a superconducting composite. The vacuum baking described herein may also be beneficially used with other techniques that may leave traces of water or other liquids on the surface of a superconducting composite, such as some of the reducing techniques described in commonly assigned "Separating layer for Heat Treating Superconducting Wire," (attorney docket 0019696-0155), filed on even day herewith and incorporated herein by reference.

Other embodiments of the invention will be apparent to those skilled in the art from a consideration of the specification or practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with the true scope and spirit of the invention being indicated by the following claims.

What is claimed is:

1. A method of preparing a superconducting composite for coating with a liquid, the superconducting composite comprising superconducting filaments embedded in a matrix, comprising:
   removing a thin layer of the matrix material to expose a surface having a low concentration of foreign particles.

2. The method of claim 1, wherein removing the layer of matrix material comprises chemical etching.

3. The method of claim 2, wherein the matrix material comprises silver, and wherein etching comprises holding the material for an effective period of time in a solution comprising nitric acid.

4. The method of claim 3, wherein the solution further comprises an effective amount of ammonium bifluoride.

5. The method of claim 2, wherein etching comprises holding the material for an effective period of time in a solution comprising an effective concentration of chloride or fluoride ions.

6. The method of claim 5, wherein the solution comprises nitric acid, hydrochloric acid, hydrofluoric acid, sulfuric acid, ferric chloride, ammonia, caustic solutions, and mixtures thereof.

7. The method of claim 1, wherein removing a thin layer comprises removing a layer of at least 0.013 mm.

8. The method of claim 1, wherein removing a thin layer does not degrade the critical current of the superconducting composite by more than 10%.

9. The method of claim 1, wherein the exposed surface has a wettability in solder of at least 250 μN/mm.

10. The method of claim 1, wherein the exposed surface has a wettability in solder of at least 300 μN/mm.

11. The method of claim 1, wherein the exposed surface has a wettability in solder of at least 350 μN/mm.

12. The method of claim 1, wherein removing a thin layer comprises electrolytic cleaning of the matrix.

13. The method of claim 12, wherein the cleaning is accomplished by immersing the superconducting composite into an electrolyte comprising a material selected from the group consisting of nitric acid, hydrochloric acid, hydrofluoric acid, sulfuric acid, sodium hydroxide, ferric chloride, ferrous chloride, ferric fluoride, ferrous fluoride, and mixtures thereof.

14. The method of claim 1, wherein the exposed surface is 97% free of particles.

15. The method of claim 1, wherein the exposed surface is 99% free of particles.

16. The method of claim 1, wherein the exposed surface is 99.5% free of particles.

17. The method of claim 1, wherein the exposed surface is 99.8% free of particles.

18. The method of claim 1, further comprising:
exposing the superconducting composite to an environment adapted to remove liquids from the exposed surface;

19. The method of claim 18, wherein exposing the superconducting composite comprises exposing the superconducting composite to a vacuum.

20. The method of claim 19, wherein exposing the superconducting composite comprises exposing the superconducting composite to a pressure of about 10 millitorr and a temperature between about 100°C and about 200°C.

21. The method of claim 18, wherein exposing the superconducting composite comprises exposing the superconducting composite to an inert atmosphere.

22. A method of preparing a superconducting composite for encapsulation, the superconducting composite comprising superconducting filaments and a protective matrix, comprising:
exposing the superconducting composite to an environment adapted to remove liquids from the composite.

23. The method of claim 22, further comprising:
immersing the superconducting composite at least partially in a liquid solution prior to exposing the composite to the liquid-removing environment.

24. The method of claim 22, wherein exposing the superconducting composite comprises exposing the superconducting composite to a vacuum.

25. The method of claim 24, wherein exposing the superconducting composite comprises exposing the superconducting composite to a pressure of about 10 millitorr and a temperature between about 100°C and about 200°C.

26. The method of claim 22, wherein exposing the superconducting composite comprises exposing the superconducting composite to an inert atmosphere.

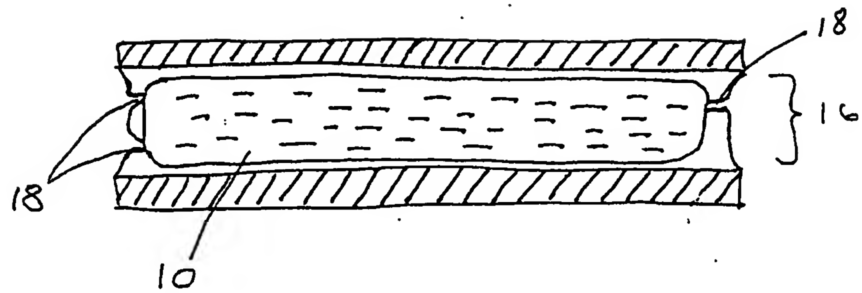

Figure 1a

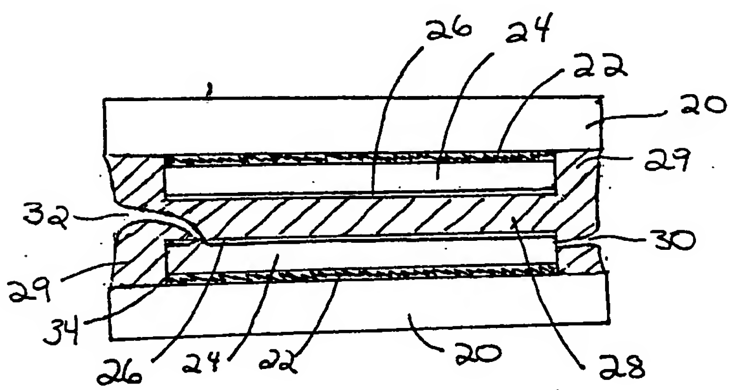

Figure 1b

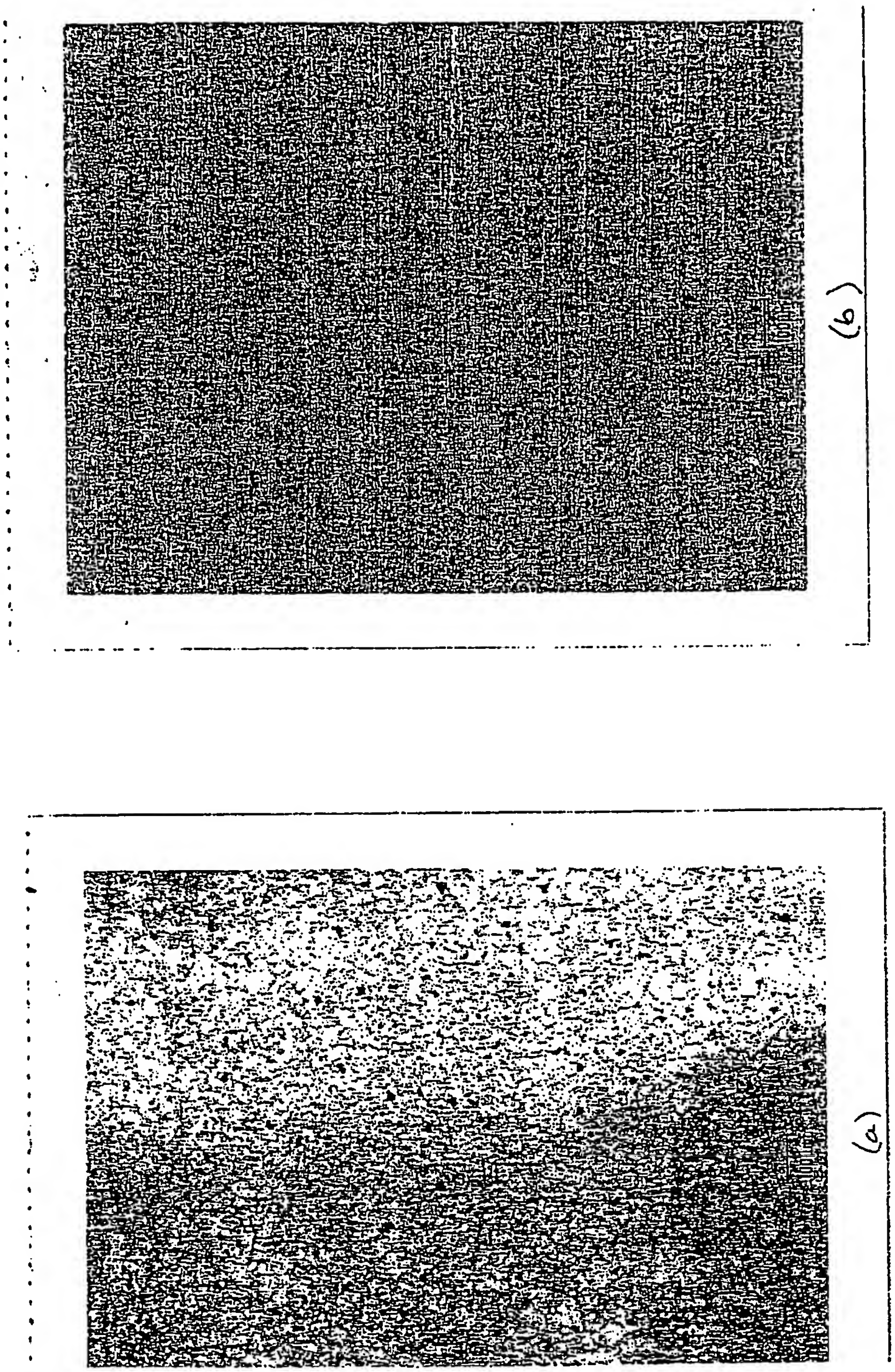

Figure 2

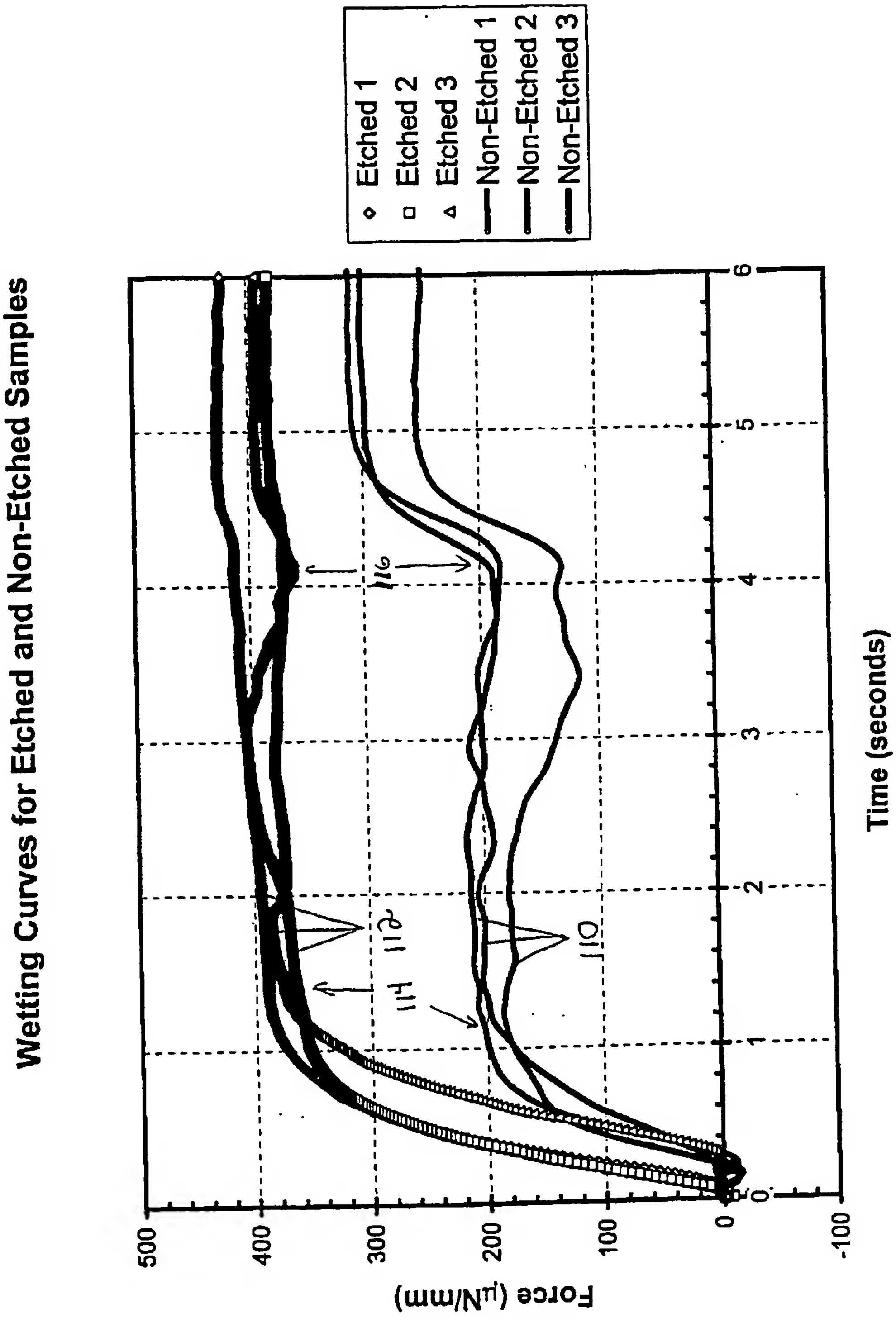
Wetting Curves for Etched and Non-Etched Samples
Etched 1
Etched 2
Etched 3
Non-Etched 1
Non-Etched 2
Non-Etched 3
Force (μN/mm)
500
400
300
200
100
0
-100
Time (seconds)
0
1
2
3
4
5
6
110
112
114
116

Figure 3

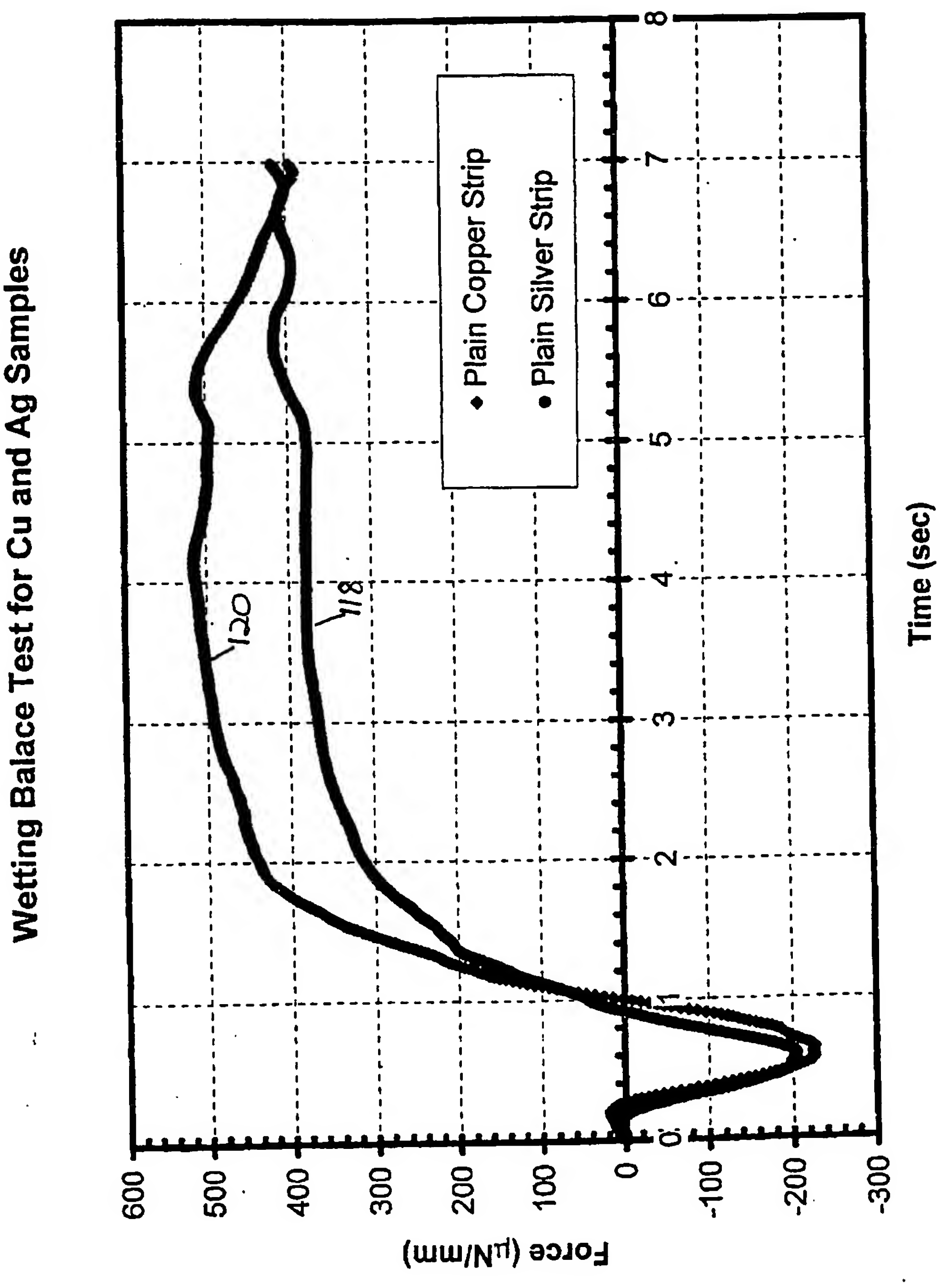
Wetting Balace Test for Cu and Ag Samples
Plain Copper Strip
Plain Silver Strip
120
118
Force (μN/mm)
600
500
400
300
200
100
0
-100
-200
-300
0
1
2
3
4
5
6
7
8
Time (sec)

Figure 4

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☑ FADED TEXT OR DRAWING
- ☑ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: ______________________________

IMAGES ARE BEST AVAILABLE COPY.
As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.